환상 지방족 Isocyanate(H₁₂MDI)와 Polyol과의 반응 속도론

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Kinetics of the Reactions between a Cycloaliphatic Diisocyanate(H₁₂MDI) and Polyols

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요 약 : N-methyl-2-pyrrolidone(NMP) 용매하에서 dibutyltin dilaurate(DBT)를 촉매로, 50~80℃ 범위에서 methylene bis(4-cyclohexyl isocyanate) (H₁₂MDI)와 polyhexamethylene carbonate glycol (PHC), polytetramethylene adipate glycol(PTAd) 및 polypropylene glycol(PPG)과의 반응을 행하여, 이들 반응의 속도상수 및 활성화 에너지를 구하였다. 또한 특정 모델 반응에 대하여 [NCO]/[OH] 비, polyol의 분자량, 촉매의 종류 및 함량이 반응에 미치는 영향을 검토하였다.

Abstract : Basic kinetic data of reactions between methylene bis(4-cyclohexyl isocyanate)(H₁₂MDI) and polyhexamethylene carbonate glycol(PHC), polytetramethylene adipate glycol(PTAd), and polypropylene glycol(PPG) in N-methyl-2-pyrrolidone(NMP) with dibutyltin dilaurate(DBT) catalyst were obtained at 50~80℃. The effects of [NCO]/[OH] ratio. molecular weight of polyol, catalyst type and amount were examined from specific model reactions.

INTRODUCTION

Due to the importance of urethane technology, reactions between isocyanate and alcohols have extensively been studied for a long time.[1~9] With regard to the kinetics and mechanism of the reaction, the effects of solvent, catalyst, and temperature were the major concern.[10~14] It was generally observed that the reactions, especially with primary alcohol, follow second order kinetics, with or without catalyst, up to certain level of conversion, the level depends on the type of catalyst, reaction

temperature, [NCO]/[OH] ratio, and steric effect of isocyanate, etc.. Deviation from second order sometimes occurs due to the catalytic effect of urethane groups, but mostly due to the side reactions, notably the formation of allophanate groups.

The isocyanates often encountered in the reactions were aromatics such as 4,4′-diisocyanato diphenylmethane(MDI) and toluene diisocyanate (TDI), and works with aliphatic type, especially with cycloaliphatic one, are sparse. There has also been a special interest in the polyurethanes based on aliphatic or cycloaliphatic isocyanates, mainly

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due to their UV resistance and weatherability. In addition, extremely low reactivity of cycloaliphatic isocyanate toward water is exclusively made use of in the preparation of polyurethane dispersion. In PU dispersion, emulsification is an essential step, and chain extension is done in aqueous media. Most works in these systems have been directed toward the synthesis of novel polyurethanes for possible application, with only a limited interest on the kinetics of reaction.[10,15] This paper describes the kinetics of reactions between methylene bis(4-cyclohexyl isocyanate)($H_{12}MDI$) and polyhexamethylene carbonate glycol(PHC), polytetramethylene adipate glycol(PTAd), and polypropylene glycol(PPG) in N-methyl-2-pyrrolidone (NMP) with dibutyltin dilaurate(DBT) catalyst at 50~80℃. The effects of type and amount of catalyst, molecular weight of polyol, and [NCO]/[OH] ratio were examined for specific model reactions at 80℃.

EXPERIMENTAL

Materials

PHC(Daicel), PTAd(Dongsung Chemical) and PPG(Korea Polyol) were dried for over 5 hrs at 80 ℃, 5~10 mmHg. NMP(Aldrich) and solvents used in titration were dried over 3 Å molecular sieve for two days. Extra pure grade of $H_{12}MDI$(Mobay) and DBT was used without further purification. Other catalysts, $Zn(CH_3COO)_2 \cdot 2H_2O$, $Hg(CH_3COO)_2$, and $SnCl_4 \cdot 5H_2O$ were dried under vacuum before use.

Procedure

Reactions were conducted in a 500 ml separable round bottom, four-necked flask, fitted with a mechanical stirrer, nitrogen inlet, condenser, and pipette outlet. Reactions were carried out in a constant temperature water bath, with ±0.1℃ precision. Polyol and catalyst solutions were fed to the reactor and heated to the reaction temperature. In a separate flask, $H_{12}MDI$ solution was heated to the reaction temperature, and added into the reactor(t=o). At desired time intervals, approximately

0.5 ml of the reaction solution was taken and quenched in ice water, and diluted in toluene(approx. 25 ml). The content of unreacted NCO was determined by the standard dibutylamine back titration method.[16] That is, an excess amount of 0.1 N n-butylamine solution(25ml) was added to the sample to react the NCO groups off, and the remaining amine groups were determined by back titration using 0.1 N HCl solution with bromophenol blue :

$$\% \text{ NCO} = 4.202 \ [(v_1 - v_2) \ n]/m \qquad (1)$$

where v_1 and v_2 are ml of HCl used with and without the sample respectively, n is the normality of HCl, and m is the weight of sample in g.

RESULTS AND DISCUSSION

Relative Reactivity and Activation Energy

Basic kinetic data described in this section were obtaind in NMP with DBT catalyst and [NCO]/[OH]=1, at 50, 60, 70 and 80℃. Typical plots of conversion vs. reaction time are shown in Fig. 1 for $H_{12}MDI$-PHC system. For the same system, a second order plot for equimolar reaction(eq. 2)
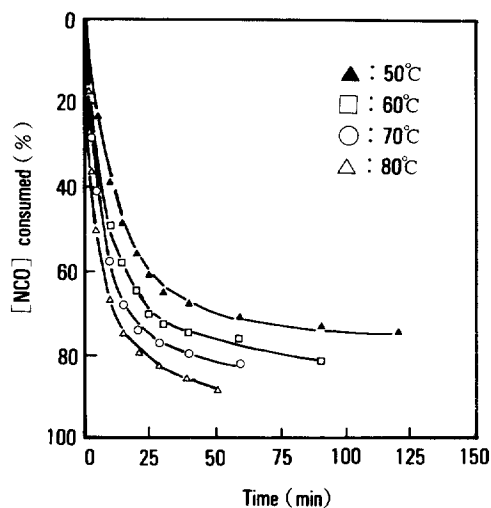

Fig. 1. Change of NCO concentration with time for the reaction of $H_{12}MDI$ with PHC at various temperature : [DBT]=6.8×10⁻⁴ mole/l, [NCO]/[OH]=1.0.
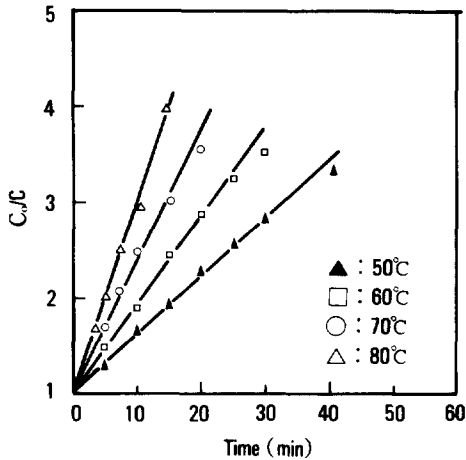
Fig. 2. Equimolar second order plot of Fig. 1.

was prepared and given in Fig. 2 :

$$C_0/C = kC_0t + 1 \qquad (2)$$

where C_0 and C are the concentrations of isocyanate at $t=o$, and $t=t$ respectively. It is seen from the figure that a drift from the second order kinetics appears as the reaction proceeds, and the time at which deviation is apparent comes earlier at higher temperature. Following the literature[17] concerning the reaction between isocyanate and alcohol, deviation from second order is mainly due to the reaction between isocyanate and urethane groups leading to allophanate. The formation of allophanate group is preferred at higher temperature as our results and earlier investigater[18] indicated. In addition, at higher temperature, urethane forming reaction proceeds rapidly, and therefore more of urethane linkages are formed at the same level of reaction. The increased concentration of urethane linkage should accelerate allophanate reaction. Using the rate constant of Fig. 2, an Arrhenius plot is prepared in Fig. 3 for the same system, including the other three of the system, and the results are summarized in Table 1. For three of the polyols used, the activation energy of the overall reaction (ΔE) is in the increasing order of PHC(8.1 kcal/mole) ⟨PTAd(9.8) ⟨PPG(11.7), which is the reverse of relative reactivity under the experimental conditions considered. The ure-
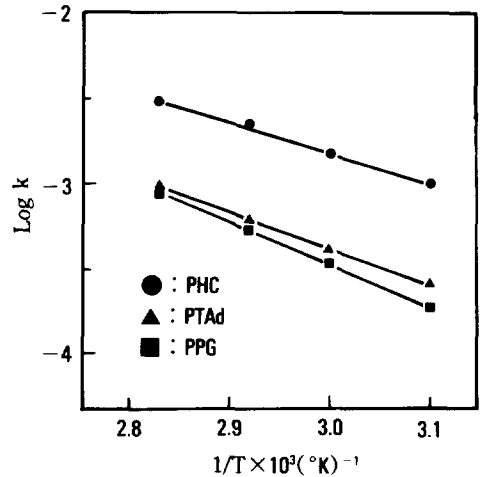

Fig. 3. Arrhenius plots of Fig. 1.

Table 1. Comparison of the Reaction Rate and Activation Energy for the Reaction between H_{12}MDI and Various Polyols in NMP : [NCO]/[OH] = 1.0, [DBT] = 6.8×10^{-4}mol/l

Polyols	Reaction Temp.(℃)	Rate Constant $k \times 10^5$ (l/mol · sec)	Activation Energy (Kcal/mol)
PHC	50	101.8	8.1
	60	141.2	
	70	235.3	
	80	305.1	
PTAd	50	25.8	9.8
	60	43.0	
	70	62.6	
	80	97.8	
PPG	50	18.8	11.7
	60	34.4	
	70	53.2	
	80	90.8	

thane forming reaction from isocyanate and alcohol is essentially neucleophilic attack of oxygen of alcohol to carbon atom of isocyanate, followed by hydrogen transfer to nitrogen.[3] Therefore the reaction is preferred with increasing nucleophilicity of alcohol. In addition, it depends also on the electron effect, chain flexibility and steric effect. The highest reactivity of PHC is probably due to the sy-

ingly exhibits a smaller pure water flux.

Acetone, in this study, is one of the representative volatile solvents, and is believed to enhance the supersaturation of CA molucules in the top layer of cast film through quantitative loss by its preferential evaporation. The critical nucleus size will be decreased as polymer supersaturation is progressed. A smaller nucleus size will produce a higher density of nuclei. Also, higher polymer supersaturation produces higher local polymer concentration in the top of cast film. At this time, the nuclei density becomes very high. This will result in a finely dispersed structure which makes the dense surface skin of resulting CA membrane as shown in Fig. 1(a)-(b) and Fig. 2(a)-(b).

On the other hand, large voids are observed in the membrane substructure in these figures. The formation of large void may result from the drastic inter-diffusion of DMF and coagulating water having their large chemical potential difference. By convective flowing,[12] void will grow faster than polymer coagulation front due to facillitated diffusion. And this phenomenon seems to be progressed in a case of a larger volume fraction of DMF. Also, membrane porosity seems to be increased in this case with increasing DMF volume fraction. This trend is well-explained in a series of SEMs in Fig. 2.

Fig. 2(a)-(b) shows the cross-sectional views of membrane prepared with smaller volume fractions of DMF. These membranes have sponge-like substructure without a void. In these membranes, skin surface will be formed densely due to the preferential evaporation of relatively larger portions of acetone. This denser surface skin can act as a mechanical barrier against drastic exchange of solvent and coagulating water. Instead of drastic void propagation, liquid-liquid phase separation will occur predominantly in the membrane substructure ; liquid droplets will form final pores, while concentrated CA polymer phases will form membranematrix through gelation.

Particularly, all voids observed in Fig. 1 and Fig. 2 have porous inner lining surfaces. Coagulating

water penetrating into the membrane is gradually diluted by mixing with solvent remaining in the membrane. Thus the coagulating behavior of water will become much meager at growing void interior. At the initial step of void formation, the boundary of void will be fluid state. Coalescence of small droplets from liquid-rich phase is possible. Therefore, many pores on the inner lining surface of void will be formed.

The Effect of Solvent Evaporation Period

Solvent evaporation period is important during membrane preparation in a view that this period can vary the concentration gradient from the top to the bottom across the entire membrane and subsequent structural asymmetry. It has been well-known that, in asymmetric cellulose acetate or polysulfone membranes, membrane permeability is gradually lowered, while solute rejection is enhanced with the increasing evaporation period.[13,14] In this research, however, the obtained results were only partially accorded with those of the previous reports.[13,14]

It can be seen from Table 4 and Table 5 that, in the course of the entire solvent evaporation period investigated, membrane performance are varied with a diverging point. Pure water flux was decreased initially and then increased afterwards with the increasing period. Solute rejection showed opposite result which was an initial increase followed by a decrease with the increasing period. These results are very noteworthy and will be discussed again through the structural interpretation in this paper.

A series of SEMs of cross-sectional views of membranes prepared with various solvent evaporation periods are listed in Fig. 3. Surface skin is more obvious in the membrane with evaporation period of 4 or 5 min, whose water flux showed minimum value as listed in Table 4, than any other skin in the membrane. On the other hand, the domain size of macrovoid is decreased till 4 min, and then turned to be increased.

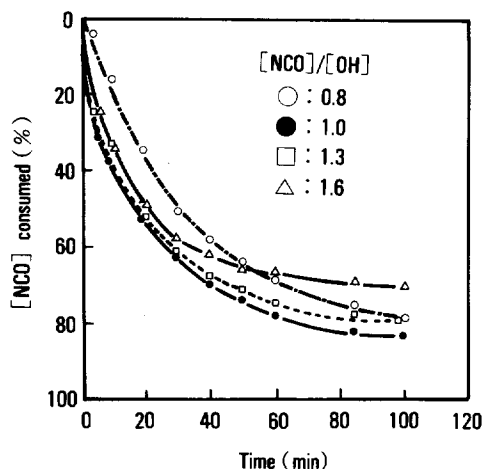Acetone seems to be evaporated very preferentially up to about 4 or 5 min, and contributed to

Fig. 4. Change of NCO concentration with time for the reaction of $H_{12}MDI$ with PPG with varying [NCO]/[OH] ratio at $80℃$: [DBT] $= 6.8 \times 10^{-4}$ mole/l.

Fig. 5. Second order plots of Fig. 4.

nergistic effect of ester and ether group, whereas the lowest reactivity of PPG due to steric hinderance of side chain and secondary alcohol effect.

Effect of [NCO]/[OH] Ratio

The effects were examined with PPG at $80℃$ using DBT catalyst with [NCO]/[OH] ratio from 0.8 to 1.6. Fig. 4 shows the concentration of NCO as a function of reaction time, and the second order plot with stoichiometric imbalance is shown in Fig. 5 :

$$\frac{1}{[NCO]_o-[OH]_o} \ln \frac{[OH]_o[NCO]}{[NCO]_o-[OH]_o} = kt \qquad (3)$$

where subscript "O" designates the initial concentration of NCO. It is seen in Fig. 5 that the deviation from linearity of second order plot occurs earlier as the ratio becomes larger. This may be interpreted as follows. With excess amount of NCO to alcohol, more of allophanate reaction with increased rate of overall reaction is expected from eq. (4).[18]

$$-\frac{d[NCO]}{dt} = k_1[NCO][OH] + k_2[NCO][NHCOO] \qquad (4)$$

Following Anzuino et al,[18] who carried out reac-
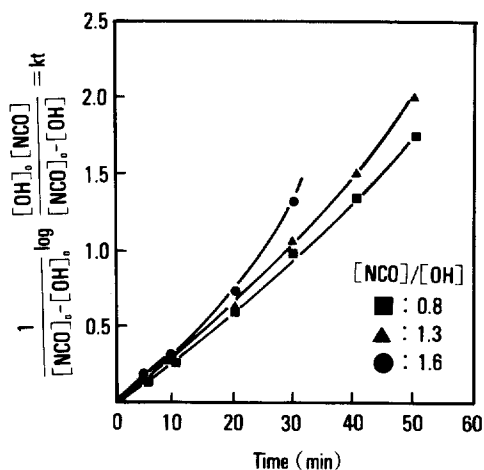
tions between MDI and 1-butanol, allophanate/urethane ratio increases with temperature, in addition to the [NCO]/[OH] ratio, and at [NCO]/[OH] $= 1.89$, the ratio increases rapidly after the deviation from second order linearity appeared.

Effect of Molecular Weight of Polyol

With PPGs of different molecular weights ranging $400 \sim 3000$, the effect of molecular weight on the reactions was studied with DBT at $80℃$. The second order plot of the reactions(Fig. 6) shows that the rate constant, within the linear region, decreases with the increase of PPG molecular weight. In polymerization reactions between bifunctional monomers, equal reactivity assumption, i. e., reactivity irrespective of molecular weight, is generally observed except the initial stage of reaction.[20] At the initial stage of reaction, say up to the degree of polymerization 3 or 4, the reactivity decreases rapidly with increasing molecular weight. The lowest PPG molecular weight used in this experiment is 400, which is presumably high enough to lie in equal reactivity range. At the same OH concentration, the viscosity will increase and hence the diffusivity will decrease with the increase of PPG molecular weight. This together with reduced solubility of PPG with the increase of molecular weight may probably cause the reduction in rate.[20] It is also noted that the deviation from the
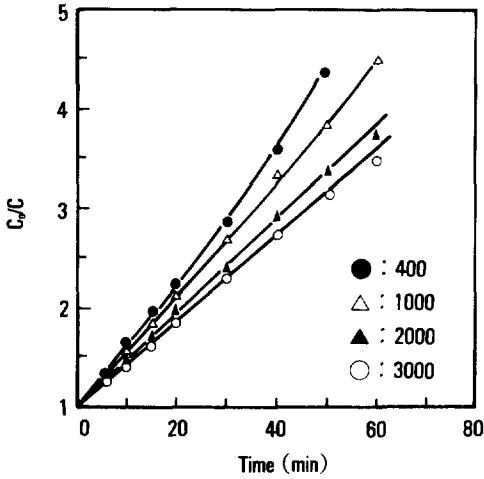
Fig. 6. Second order plots for the reaction of $H_{12}MDI$ with PPG with varying PPG molecular weight at 80°C : [DBT]=6.8×10^{-4} mole/l, [NCO]/[OH]=1.0.

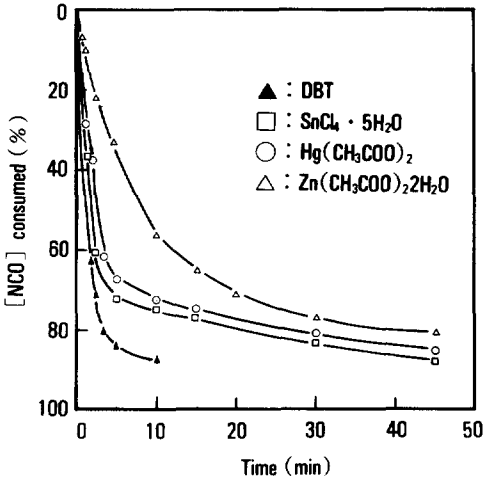**Fig. 7.** Change of NCO concentration with time for the reaction of $H_{12}MDI$ with PPG with various catalysts at 80°C : [DBT]=5.16×10^{-3} mole/l, [NCO]/[OH]=1.0.

Fig. 8. Second order plots of Fig. 7.

Fig. 9. Change of the reaction rate for the reaction of $H_{12}MDI$ with PPG with various [DBT] at 80°C : [NCO]/[OH]=1.0.

second order linearity appears earlier with lower molecular weight of polyol, due probably to the rapid primary reaction, and consequently to the allophanate reaction.

Effect of Catalyst Type and Concentration

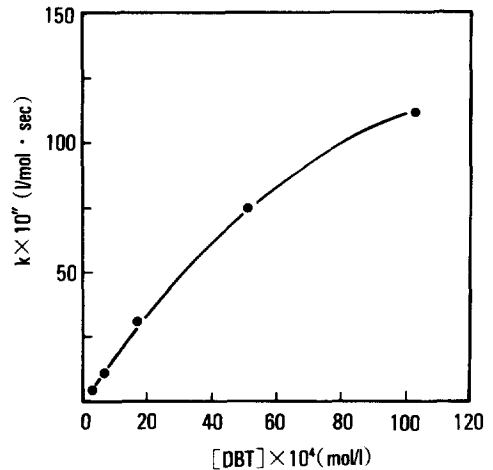Fig. 7 shows that DBT is most effective catalyst for the model reactions considered, and the cataly-

tic activity is in the increasing of order of Zn $(CH_3COO)_2 \cdot 2H_2O$ < $Hg(CH_3COO)_2$ < $SnCl_4 \cdot 5H_2O$ < DBT. When the second order plot is prepared (Fig. 8), it is also seen that DBT induces the secondary reaction at the lowest conversion, whereas the other metallic salts almost exclusively drive primary reaction. Essentially identical results were also reported for the reactions between hexamethylene diisocyanate (HDI) and n-Butanol in dimethyl acetamide by Anzuino et al.[21]

Fig. 9 shows the effect of catalyst(DBT) concentration on overall reaction. In reactions between isocyanates and alcohols with metallic salt catalyst, complex is first formed with polyol, followed by reaction with isocyanate.[7~9] With more catalyst, more of complex formation is preferred, and the similar results are expected.

CONCLUSIONS

The urethane forming reactions between H_{12}-MDI and PHC, PTAd and PPG with DBT catalyst in 50~80℃ generally followed the second order kinetics, except the last stage of reaction especially at higher temperature, with activation energies, 8.1 (PHC), 9.8(PTAd), and 11.7(PPG) kcal/mole. Deviation from the second order kinetics appeared earlier as the [NCO]/[OH] ratio increased in reaction with PPG with DBT catalyst. Reaction rate decreased rapidly with the increase of PPG molecular weight. In reactions with PPG, the catalytic activity for the overall reaction was in the increasing order of $Zn(CH_3COO)_2 \cdot 2H_2O \langle$ Hg $(CH_3COO)_2 \langle SnCl_4 \cdot 5H_2O \langle DBT$, and DBT induced secondary reaction at the lowest conversion.

REFERENCES

1. J. W. Baker, and J, J. Gaunt, *J. Chem. Soc.*, 19 (1949).

2. J. W. Baker, and J, J. Gaunt, *J. Chem. Soc.*, 27 (1949).

3. J. W. Baker, and J, B. Holsworth, *J. Chem. Soc.*, 713 (1947).

4. R. P. Tiger and S. G. Entelis, *Kinetikai Kataliz*, 6, 554 (1965).

5. S. Ephraim, A. E. Woodword, and R. B. Mesro-
bian, *J. Am. Chem. Soc.*, 80, 1326 (1958).

6. A. A. Zaplatin, F. Samigullin, V. V. Zharkov, L. N. Nikitina, and K. P. Kafeengauz, *Kinet. Catal.*, 16, 1223 (1975).

7. A. E. Oberth, and R. S. Bruenner, *J. Phys. Chem.*, 72, 8540 (1968).

8. R. B. Moodie, and P. J. Sansom, *J. Chem. Soc. Perkin Trans.* II, 664 (1981).

9. A. Farkas, and P. F. Strohm, *Ind. Eng. Chem. Fundam.*, 4, 32 (1965).

10. J. H. Saunders and K. C. Frisch, "Polyurethanes : Chemistry and Technology", High Polymer Series, X VI, Wiley-Interscience, New York, Part I, 1962, and Part II, 1964.

11. R. W. Lenz, "Organic Chemistry of Synthetic High Polymers", Wiley-Interscience, New York, 1967.

12. C. Hepburn, "Polyurethane Elastomers", Applied Science, London, 1982.

13. D. C. Allport and W. H. Janes, "Block Copolymers", Applied Science, London, 1973.

14. D. J. Lyman, *J. Polym. Sci.*, 45, 49 (1960).

15. I. Yilgor, E. H. Orhan, and B. M. Baysal, *Makromol. Chem.*, 179, 109 (1978).

16. D. J. David and H. B. Staley, "Analytical Chemistry of Polyurethanes", High Polymer Series, X VI, Part III, Wiley-Interscience, New York, 1969.

17. I. Yilgor and E. Mcgrath, *J. Appl. Polym. Sci.*, 30, 1733 (1985).

18. G. Anzuino, A. Pirro, G. Rossi, and L. Polo Friz, *J. Polym. Sci., Polym. Chem. Ed.*, 13, 1657 (1975).

19. O. Levenspiel, "Chemical Reaction Engineering", Part II, Tower Press, 1972.

20. G. G. Odian, "Principles of Polymerization", John Willey & Sons, New York, 1981.

21. G. Anzuino, A. Pirro, G. Rossi, and L. Polo Friz, *J. Polym. Sci., Polym. Chem. Ed.*, 13, 1667 (1975).